The Nature of the Bonding in Some P–N, As–N, and S–N Compounds

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Summary The ^{15}N–^{1}H coupling constants in some aminophosphines, aminoarsines, and sulphenamides have been determined.

AMINOPHOSPHINES,[1] aminoarsines,[1] and sulphenamides[2] have recently been found to possess substantial torsional barriers about the N–X bonds (X = P, As, or S). Furthermore, an *X*-ray crystallographic study[3] of the aminophosphine, $(CH_3)_2NPF_2$, has revealed a trigonal planar geometry about nitrogen and an unexpectedly short P–N bond distance. These findings have raised two important but related questions: (a) is trigonal planar nitrogen a general structure feature of aminophosphines, aminoarsines, and sulphenamides? and (b) what is the importance of multiple bonding in the N–X bonds of these compounds? We present some new ^{15}N–H spin coupling data which are relevant to these questions.

The appropriate ^{15}N-labelled compounds (Table) were prepared by substituting 96·5% enriched $^{15}NH_3$ for $^{14}NH_3$ in the syntheses described in the literature. The experimental scalar ^{15}N–H couplings have been related to the percentage 2*s* character in the nitrogen bonding orbitals by the phenomenological equation of Binsch *et al.*[4]

$$\% \; 2s = 0{\cdot}43 \; J(^{15}N\text{–}H) - 6$$

These results suggest that the nitrogen atoms are approximately trigonal planar in $(CF_3)_2PNH_2$, $[CF_3S]_2NH$, and the phosphorane $PF_3(NH_2)_2$. On the other hand, the aminoarsines, the methyl-substituted aminophosphines, and

CF_3SNH_2 are predicted to possess approximately tetrahedral geometry at nitrogen. Thus, from a purely electronic standpoint, planar geometry at nitrogen is expected for N–P and N–S compounds with strongly electronegative substituents at phosphorus or sulphur.

TABLE

Compound	$J(^{15}N–H)$	Nitrogen %2*s*
$(CF_3)_2PNH_2$	85·6	30·8
$PF_3(NH_2)_2$	87·5	31·6
$CF_3CH_3PNH_2$	78·9	27·9
$[CF_3CH_3P]_2NH$	77·4, 78·9[a]	27·3, 27·9
$(CF_3)_2AsNH_2$	73·4	25·6
$[(CF_3)_2As]_2NH$	79·0	28·0
CF_3SNH_2	80·6	28·7
$[CF_3S]_2NH$	99·1	36·6

[a] The observation of two $J(^{15}N–H)$ values is due to the phosphorus chiral centres.

Our data are consistent with the π-bonding hypothesis in that attachment of electronegative groups to phosphorus or sulphur contracts and lowers the energy of the 3*d*-orbitals, thus facilitating $2p_\pi–3d_\pi$ bonding.[5]† This interaction is maximised when the nitrogen geometry is planar and the lone pair resides in a pure 2*p*-orbital. In this model π-bonding should not be as important in aminoarsines because of the less effective overlap of the 2*p* nitrogen orbital with the 4*d* arsenic orbitals. The large $J(^{15}N–H)$ in $PF_3(NH_2)_2$ is indicative of appreciable π-bonding in the equatorial sites of a trigonal bipyramid.‡ This conclusion is consonant with molecular orbital calculations on the phosphorus(V) chlorofluorides.[6] Our results can also be interpreted in terms of a σ-bonding model, *viz.* in the structures XNH_2 and X_2NH increasing the electronegativity of X diverts more 2*s* character into the N–H bonds[7] and thereby increases the Fermi contact contribution to $J(^{15}N–H)$. On this basis the inferred order of group electronegativity towards the NH_2 moiety is $(NH_2)PF_3 > (CF_3)_2P > CF_3S > CF_3CH_3P > (CF_3)_2As$.

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† Most discussions of π-bonding have related to the use of the vacant 3*d*-orbitals of *e.g.*, P or S. However, derived valence state ionisation potential data indicate that, for neutral atoms, the 4*p*- and 3*d*-orbitals are very close in energy. Consequently, $2p_\pi–4p_\pi$ bonding may be as important as $2p_\pi–3d_\pi$ bonding. See L. C. Cusachs and J. R. Linn, *J. Chem. Phys.*, 1967, **46**, 2919.

‡ The ^{19}F n.m.r. data are best interpreted in terms of a trigonal bipyramidal structure with equatorial NH_2 groups. See M. Lustig and H. W. Roesky, *Inorg. Chem.*, 1970, **9**, 1289.

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